WORKPLAN FOR DNAPL CHARACTERIZATION AND REMEDIATION STUDY

Sauget Area 1
Sauget, Illinois

Submitted to
Solutia Inc.   February 28, 2003

Groundwater Services, Inc.
2211 Norfolk, Suite 1000, Houston, Texas 77098

WORKPLAN FOR DNAPL CHARACTERIZATION AND REMEDIATION STUDY
Solutia, Inc., Sauget Area 1 Sites, Sauget, Illinois

1.0   INTRODUCTION

As requested by Solutia, Groundwater Services, Inc. (GSI), has prepared this workplan for a characterization and remediation study of dense non-aqueous phase liquids (DNAPLs) in the subsurface underlying the Sauget Area 1 Sites in Sauget, Illinois. The study focuses on Sauget Area 1 Sites G, H, and I.

EPA Letter

This workplan addresses the issues presented in the U.S. EPA's letter to Solutia dated January 9, 2003, where a DNAPL study was requested with these focus areas:

The characterization and distribution of DNAPL within the middle and deep hydrogeologic units, the assessment of DNAPL migration under current and future site conditions, and the risk of uncontrolled DNAPL mobilization.

The extent and properties of DNAPL (e.g., density, viscosity, and interfacial tension); as well as the timing of the DNAPL release; topography, property, and heterogeneity of geologic units on which the DNAPL may accumulate; the existence of ongoing DNAPL releases; and transport characteristics of the bedrock.

The evaluation of the DNAPL remedial options and the evaluation of the benefits and costs associated with source removal technologies (thermal technologies such as steam injection and chemically-enhanced extraction such as the use of surfactants or co-solvents).

The proposed work program includes: an initial survey for DNAPL in existing wells, subsurface soil sampling and testing, piezometer installation, DNAPL recovery tests, laboratory testing of DNAPL samples, bench-scale treatability tests, evaluation of source depletion alternatives, evaluation of remedial alternatives, and development of a project report.

Historical information indicates that liquid waste disposal was conducted at Sites G, H, and I. For this reason, these three sites were selected for the DNAPL investigation. Site L was used as a tank truck washout lagoon, with an overflow to Dead Creek, and Site N was used for disposal of construction rubble. DNAPL investigation is not proposed for Sites L and N because DNAPL is not expected at these two sites, given the nature of historical operations.

Previous Source Evaluation Study

Solutia investigated source mechanisms at Sauget Area 1 in a report issued by GSI on May 21, 2001. A copy of the report is attached with this workplan. The report, which was presented as Appendix C in the Sauget Area 1 Engineering Evaluation/Cost Analysis and Remedial

GROUNDWATER
SERVICES, INC.

Investigation/Feasibility Study (the EE/CA and RI/FS Report), focused on Site I and addressed two issues:

1) *What is the dominant source mechanism at the site?*

2) *What is the effect of an intensive pump-and-treat system on the lifetime of the source?*

The report concluded that *DNAPL dissolution* is a major source mechanism at Site I based on several indicators, most importantly: 1) dissolved constituent concentrations increase with depth, 2) site constituents extend from the water table to the bottom of the water-bearing interval, and 3) three constituents are found at concentrations that suggest the possible presence of DNAPL. Some leaching of unsaturated waste/soil materials may also be occurring, as some constituents did not show increasing concentrations with depth. Overall, however, DNAPL dissolution appears to be the dominant source mechanism at Site I.

If DNAPL dissolution is the dominant source mechanism at Site I, it is likely that the DNAPL in the unconsolidated valley fill deposits is present as thin vertical fingers and small horizontal pools throughout the entire vertical extent of the water-bearing unit.

A planning level source lifetime calculation was done to estimate the relative performance of various pumping schemes on removing DNAPL from the fill deposits. This analysis, while not providing high-confidence estimates of the absolute time to cleanup, indicates that with an assumed mass of 410,000 kg of VOCs and SVOCs in the saturated zone below Site I, intensive groundwater pumping over a 10 to 30 year period does not appear to have an appreciable effect on overall source lifetime (i.e., ≤ 10% reduction).

The source evaluation study for Sauget Area 1 provides the basis for the elements in this workplan for a DNAPL characterization and remediation study.

2.0 WORKPLAN TASKS

Task 1: Project Startup

Prior to the start of the field program, GSI will review the existing Sauget Area 1 Health and Safety Plan to confirm that it addresses all anticipated field activities that are included in this work program, including drilling and sampling in Level B personal protective equipment. Amendments to the Health and Safety Plan, if any, will be completed and reviewed by Solutia prior to the start of field activities.

Task 2: Initial Survey for DNAPL at Existing Wells

A survey will be conducted to check for the possible presence of DNAPL in approximately 35 existing monitoring wells located at and near the Area 1 sites. At each well, the DNAPL survey will include measurement of the depth to water and a check for the presence and thickness of DNAPL using an electronic interface probe. A visual check for DNAPL will be performed at each well by lowering a weighted cotton string to the bottom of the well, then retrieving the string to inspect for evidence of staining. Finally a disposable Teflon bailer will be lowered to the bottom of each well to check for the presence of accumulated DNAPL. New string, bailer, and bailer cord will be used for each well, and soiled string, bailers, and cord generated during the survey will be placed in a designated container for management by Solutia. All field activities and laboratory programs associated with Tasks 2, 3, and 4 of this workplan will be conducted in accordance with the Sauget Area 1 Field Sampling Plan and Quality Assurance Project Plan.

One location from within each of the three fill areas (Sites G, H, and I) will be selected for soil sampling and piezometer installation (Task 3). The selected locations for the borings will correspond to the well locations with the maximum measured DNAPL thickness.

Task 3: Soil Sampling and Installation of Piezometers

The goals of Task 3 are: i) to characterize the residual and free-phase DNAPL potentially present within the fill areas and within the upper, middle, and deep hydrogeologic units; ii) to confirm depth to bedrock; and iii) to investigate for the possible presence of pooled DNAPL at and near the bedrock surface. For this task, continuous soil coring will be conducted using the sonic drilling method at the three locations identified based on results of Task 2. The proposed locations will include one boring each at Sites G, H, and I. Each boring will be continuously cored through the fill materials, the alluvial deposits, and five feet into bedrock, to an estimated total depth of 110 feet below grade.

Soil Core Examination: During drilling, a 4-inch diameter core barrel will be advanced to collect continuous soil cores. A 6-inch diameter steel over-ride casing will be advanced over the inner drill rods and core barrel to stabilize the borehole and minimize cross-contamination between intervals. In addition, a 7-inch diameter over-ride casing will be used to isolate the fill materials. After retracting each core barrel from the borehole, the core will be extruded into a plastic sleeve for examination and screening. The supervising geologist/engineer will scrape the outer surface of the core, examine the core to determine soil classification, and look for visual evidence of contamination, such as staining, NAPL droplets, or a sheen. The surface of the core will be briefly screened by a photo-ionization detector (PID) to check for elevated levels of organic vapors prior to collection of a soil sample.

Selection of Soil Samples for Laboratory Testing: One soil sample from each 10-foot length of core will be retained for laboratory analysis. Duplicate soil samples will be collected at a ratio of one per ten soil samples, and matrix spike/matrix spike duplicate pairs will be collected at a ratio of one set per twenty soil samples. If visible evidence of NAPL is noted in a soil core, the soil

sample retained for laboratory analysis will be collected from the portion of the core that has the most obvious visual indications of NAPL. If there are no visual indications of NAPL, the soil sample for laboratory analysis will be collected from an interval exhibiting noticeably higher organic vapor levels than the rest of the core, as measured by scanning the surface of the core with the PID. If PID readings are relatively uniform across the surface of the core, then the soil sample will be taken from approximately the midpoint of the core.

Analytical Program for Soil Samples: Samples will be placed in appropriate containers, stored on ice, and shipped to Severn Trent Laboratories (STL) in Savannah, Georgia. STL will test each soil sample for TOC, VOCs, and SVOCs. TOC analyses will be used to determine the total mass of organic constituents in each soil sample. VOC and SVOC analyses will be used to chemically characterize the organic constituents present in the soil samples. VOCs and SVOCs were selected as analytical parameters for chemical analyses because groundwater data collected during the Sauget Area 1 Support Sampling Plan indicate that these are the most mobile constituents in groundwater at Sites G, H, and I. These data will be analyzed to obtain an estimate of DNAPL saturation (percent of pore space containing DNAPL) for each sampling point. Estimated values of porosity and fraction organic carbon (foc) will be used for these calculations.

Additional sample containers will be placed on dry ice and submitted to PTS Laboratories in Houston, Texas for analysis of pore fluid saturations using a modified version of the Dean-Stark test procedure (API RP 40). The Dean-Stark test results will provide a direct measurement of DNAPL saturation that can be used as an independent verification of the calculation approach using the VOC, SVOC, and TOC test results.

Installation and Development of Piezometers: After reaching the target depth, each boring will be completed as a piezometer to investigate the presence and thickness of DNAPL. The piezometers will be screened both above and below the bedrock surface and will be constructed of 2-inch diameter PVC casing with 15 ft of stainless steel wire-wound screen. After the screen and casing are installed in the borehole, the sandpack, bentonite seal, and grout seal will be placed as the six-inch diameter over-ride casing is retracted from the borehole. Each piezometer will be developed by air-lift pumping, bailing, or another approved method. Following completion of development, the depth to water and total depth of each piezometer will be measured, and each piezometer will be checked for the possible presence of DNAPL using an interface probe, weighted cotton string, and Teflon bailer. The piezometers will then be left undisturbed for a period of at least three weeks prior to the start of Task 4, to allow for possible accumulation of DNAPL.

Management of Investigation-Derived Waste: All investigation-derived wastes generated during drilling, soil sampling, and piezometer development will be placed in designated containers for management by Solutia.

Task 4: DNAPL Recovery Tests and DNAPL Analyses

<u>DNAPL Mobility Evaluation</u>: At each of the three boring locations discussed above, one relatively undisturbed subsurface sample of contaminated fill material and one relatively undisturbed soil sample will be collected and submitted for laboratory testing for DNAPL mobility. The samples will be collected from the depth intervals where DNAPL is known or most likely to be present, based on field evidence collected during Task 3. If the cores collected during sonic drilling are disturbed and not suitable for the DNAPL mobility test procedure, direct push sampling equipment (i.e., Geoprobe) will be used to advance a separate borehole at each of the three locations. Undisturbed samples will be collected from selected depth intervals in the contaminated fill materials using acrylic tubes. The core samples will be placed on dry ice and submitted to PTS Laboratories of Houston, Texas, for evaluation of DNAPL mobility using a modified centrifuge test procedure (ASTM D425M). The test results will include initial and residual pore fluid saturations, total porosity, dry bulk density, and visual indications of produced fluids.

<u>DNAPL Recovery Tests</u>: The three piezometers installed in Task 3 will be surveyed for the possible presence of DNAPL using the interface probe, weighted cotton string, and Teflon bailer. If free-phase DNAPL is present, a DNAPL recovery test will be conducted at each of the three piezometers. Each recovery test will last approximately 8 hours and will be performed using a flow-controlled submersible pump purchased for the project. The pumping rate will be set to minimize the volume of water pumped from the well by performing a visual inspection of fluid samples collected in closed flasks. The volume of DNAPL and the volume of water produced will be recorded at 15-minute intervals. The volume of DNAPL and volume of water will be determined by measuring accumulations in a collection vessel such as a closed tank or drum. A sample of the DNAPL and a sample of a DNAPL/water mix will be retained from each of the three piezometers.

<u>DNAPL Analyses</u>: The three samples that consist of a DNAPL/water mix will be submitted for laboratory analysis of fluid properties at PTS Laboratories in Houston, Texas. The samples will be tested using ASTM D445 and ASTM D1481, which include measurement of: i) dynamic viscosity and fluid density at three temperatures; ii) surface tension for each fluid; and iii) interfacial tension for oil/water, oil/air, and water/air. The three samples that consist only of DNAPL will be submitted to Severn Trent Laboratories in Savannah, Georgia, for laboratory analysis of chemical composition. These samples will be analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin, and metals (including mercury).

Task 5: Bench-Scale Treatability Tests

Bench-scale treatability tests will be conducted for thermal treatment, for surfactant addition, and, if feasible, for in-situ chemical oxidation. The results from these tests will provide design information for evaluating the applicability and potential effectiveness of thermal, surfactant-based, and chemical oxidation technologies.

<u>Thermal Treatability Test</u>: Three samples of DNAPL collected during Task 4 will be analyzed to generate boiling point curves using ASTM D-86 (Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure). This test will provide boiling point data up to 750 degrees celcius. However, any tars or other material with boiling points above this range will not be measured.

Test results will indicate if temperatures that can be achieved by applicable thermal treatments (such as steam addition) can remove sufficient residual and free-phase DNAPL from the subsurface. Note that the results from this treatability test will only indicate the theoretical technical performance of thermal treatment. Practical and engineering constraints that may limit the application of the technology will be addressed in Task 6.

<u>Surfactant Treatability Test</u>: Samples of the DNAPL will be analyzed for key physical and chemical properties as part of Task 4. Using these data, a representative sample of DNAPL will be selected from available samples and used for all the surfactant bench-scale tests.

A literature review will be performed to identify promising surfactants that could be used for remediation. Key criteria for selecting the surfactants will be i) experience at other surfactant sites; ii) risk associated with addition to subsurface (i.e., a food-grade surfactant will likely be required); and iii) compatibility with local water quality conditions.

Each surfactant will be evaluated by:

1. Adding DNAPL to water in beaker or closed jar and gently mixing.
2. Sampling and analyzing the aqueous phase for VOCs and SVOCs
3. Adding surfactant slowly and mixing until the critical micelle concentration (CMC) is observed visually (i.e., by a noticeable change in appearance of the aqueous phase).
4. Analyzing post CMC aqueous phase for VOCs and SVOCs.

Each surfactant will be tested at two ionic strengths. The test results will indicate how much surfactant is required to achieve the CMC in the subsurface.

<u>Chemical Oxidation Treatability Evaluation</u>: Using data on DNAPL chemical composition taken from Task 4, calculations will be performed to determine the mass of various oxidants required to oxidize a given mass of DNAPL from the site. The calculations will be repeated at different pH values to evaluate the sensitivity of various oxidants to pH. If the design information indicates that chemical oxidation is feasible, then bench-scale oxidation tests of the most promising oxidant acting on the DNAPL will be performed to confirm the results of the calculations.

A short data report will be developed to summarize results from the bench-scale treatability tests and chemical oxidation treatability evaluation.

Task 6: Review of DNAPL Source Depletion Alternatives

An analysis of whether active DNAPL source depletion technologies are applicable to Sauget Area 1 will be conducted. The analysis will focus on three aggressive source treatment technologies: i) thermal treatment, ii) surfactant treatment, and iii) in-situ chemical oxidation.

This analysis will focus on three areas:

Performance: An assessment of the potential performance of thermal treatment, surfactant treatment, and chemical oxidation will be made using data from the bench-scale treatability tests performed as part of Task 5, and from observed performance at pilot-scale tests and full-scale tests reported at other sites. GSI will rely on a Remediation Performance Database that GSI is now developing for the Department of Defense's Strategic Research and Development Program (SERDP). In addition, GSI will rely on preliminary results presented in meetings of the Expert Panel convened by EPA to evaluate source depletion (C. Newell of GSI was a member of the Expert Panel).

Actual performance of thermal treatment, surfactant treatments, and chemical oxidation in a full-scale field application at the Sauget 1 area will be estimated. The potential for rebound of dissolved-phase concentrations and the potential need for continued management of the dissolved-phase plume after treatment will also be evaluated.

Cost: GSI will use unit costing approaches in the literature based on area, volume, and depth to develop planning-level costs for application of the three treatment approaches. For surfactants, the Advanced Applied Technology Demonstration Facility's (AATDF) design manual for surfactant treatment will be used as a primary costing resource. For thermal treatment, costs reported in the literature for full-scale applications will be developed. Costs will be adjusted to reflect site-specific conditions, such as a deep saturated unit (> 100 ft), and the need to drill through waste units.

Engineering Considerations: Practical engineering considerations such as access, safety issues, and other factors will be assessed in the application of thermal treatment, surfactant treatment, and chemical oxidation.

In addition, an analysis of the relative mass flux originating from leachate migration and from DNAPL dissolution will be performed using dissolved-phase concentration data and groundwater flowrate estimates. This analysis will indicate the relative contribution of leachate and DNAPL dissolution on the total mass flux leaving the source zone.

Task 7: Remedial Alternatives Evaluation

An updated evaluation of remedial alternatives for Sauget Area 1 will be performed based on the findings from Tasks 2 through 6 of this work program and results of previous remedial alternative analyses documented in earlier site reports. The evaluation will result in a

comparison of the costs, benefits, and engineering considerations of the following remedial alternatives:

- Natural Attenuation (from Sauget Area 1 EE/CA and RI/FS Report)
- Capping Source Areas (from Sauget Area 1 EE/CA and RI/FS Report)
- Hydraulic Barrier at Mississippi River (from Sauget Area 1 EE/CA and RI/FS Report, Sauget Area 2 Interim Groundwater Remedy FFS, and capture zone modeling of the Sauget Area 2 Interim Groundwater Remedy using a particle tracking model)
- Aggressive Pump-and-Treat at Sauget Area 1 Source Areas (Sites G, H, and I) (from Sauget Area 1 EE/CA and RI/FS Report)
- In-Situ Treatment of Source Areas and Aquifer Matrix (for the most promising source depletion alternative identified in Tasks 5 and 6 of this work program).

Task 8: Project Report

A project report will be prepared to include these elements:

- Summary of all field activities
- Profiles of DNAPL distribution vs. depth for soil borings
- Two stratigraphic cross sections
- Summary of DNAPL physical and chemical properties
- DNAPL recoverability test results and interpretation
- DNAPL mobility test results and interpretation
- Bench-scale treatability test results and interpretation
- Results from DNAPL source depletion alternatives study
- Results of remedial alternatives evaluation
- Bedrock transport analysis (based on core inspection and technical literature)
- Appendix – Bench scale treatability test data transmittals
- Appendix – Soil boring logs
- Appendix – As-built diagrams for piezometers
- Appendix – Laboratory data

3.0   SCHEDULE

It is anticipated the entire project could be completed within approximately six months of notice to proceed, in accordance with the estimated timeline outlined below.

Project Startup and Completion of Field Activities	Months 1, 2, and 3
Laboratory Analyses and Treatability Studies	Months 2, 3, and 4
Data Interpretation and Review of Source Depletion Alternatives	Months 5 and 6
Remedial Alternatives Evaluation and Project Report	Months 5 and 6

**GROUNDWATER
SERVICES, INC.**

ATTACHMENT 1

SAUGET AREA 1 SOURCE EVALUATION STUDY

May 21, 2001

SOURCE EVALUATION STUDY

Sauget Area 1

Sauget and Cahokia, Illinois

Submitted to
Solutia Inc.   **May 21, 2001**

Groundwater Services, Inc.
2211 Norfolk, Suite 1000,   Houston, Texas 77098

EXECUTIVE SUMMARY

An evaluation of the source of impacted groundwater at Site I within Sauget Area 1 was performed to evaluate two questions:

1) *What is the dominant source mechanism at the site?*
2) *What is the effect of an intensive pump-and-treat system on the lifetime of the source?*

Dominant Source Mechanism

Two source mechanisms that have the potential to be active at the Sauget site are: 1) *leaching* of unsaturated source materials, and 2) residual Dense Nonaqueous Phase Liquid *(DNAPL) dissolution* (see Figure 1). Six general indicators were evaluated to assess which of these two source mechanisms are primarily responsible for the observed plumes associated with Site I.

The analysis indicated that *DNAPL dissolution* is a major source mechanism at Site I based on an analysis of six different indicators. The following indicators support the conclusion that trapped residual DNAPL is present: dissolved constituent concentrations increase with depth, site constituents extend from the water table to the bottom of the water-bearing interval, and three constituents are found at concentrations that suggest the possible presence of non-mobile residual DNAPL. Some leaching of unsaturated waste/soil materials may also be occurring, as some constituents did not show increasing concentrations with depth. Overall, however, **DNAPL dissolution** appears to be the dominant source mechanism at Site I.

Source Conceptual Model

If DNAPL dissolution is the dominant source mechanism at Site I, it is likely that the DNAPL in the unconsolidated valley fill deposits is present as thin vertical fingers and small horizontal pools throughout the entire vertical extent of the water-bearing unit. Only a small fraction of the total DNAPL mass can ever be removed by pumping any "free-phase" DNAPL pools, if they are found. The rest of the DNAPL is immobile, and will serve as a long-term continuing source of constituents to groundwater.

The current natural mass removal rate via dissolution from the Site I source zone was estimated to be 7000 kg/yr assuming uniform source concentrations throughout the source zone.

Effect of Pumping

As shown by DNAPL dissolution expressions, increasing the flow rate through a DNAPL source zone will significantly decrease the concentration of constituents in

the extracted groundwater. For example, if the flowrate through a DNAPL source zone is increased by a factor of 8.9 (to 1500 gpm) due to intensive pumping, the resulting concentration is likely to decrease by a factor of 3.6 while pumping is active, resulting in an overall increase in the mass removal rate of only 2.5 times. Therefore, an intensive pump-and-treat system at Site I with 8.9 times the natural flowrate through the source area (an achievable pumping rate if there is no reinjection) would result in an initial mass removal rate of 17,500 kg/yr.

A planning level source lifetime calculation was done to estimate the relative performance of various remediation schemes. This analysis, while not providing high-confidence estimates of the absolute time to cleanup, does indicate that with an assumed mass of 410,000 kg of VOCs + SVOCs in the saturated zone below Site I, intensive pumping over a 10 to 30 year period does not appear to have an appreciable effect on overall source lifetime (i.e., ≤ 10% reduction). Similar limitations are expected for Sites G/H/L as well.

INTRODUCTION

As requested by Solutia Inc. (Solutia), Groundwater Services, Inc. (GSI), has completed a study of hydrogeologic, source, and fate and transport data from the Sauget Area 1 located in Sauget and Cahokia, Illinois. The study was conducted to: 1) help determine what type of source mechanisms are responsible for dissolved constituents found in the affected groundwater, and 2) determine the feasibility of remediating this source area by aggressive pumping. This letter report summarizes the results of the study.

PROJECT BACKGROUND

An extensive RI/FS study of Sauget Area 1 is now being conducted by Solutia. Data from two groundwater monitoring well transects indicates the presence of dissolved constituents migrating west in groundwater from the vicinity of one of the six source areas in Area 1 (i.e., Site I) at concentrations exceeding Illinois Class II groundwater standards.

Source Site I

Site I originally was a sand and gravel pit which received industrial and municipal wastes from 1931 to 1957. Site I is approximately 19 acres in area and underlies a large, fenced, controlled-access, gravel covered truck parking lot and the Sauget City Hall and associated parking lots (Sauget Area 1 EE/CA and RI/FS Support Sampling Plan). Soil samples collected from Site I have indicated elevated levels of volatile organic compounds (e.g., benzene, chlorobenzene); semi-volatile organic compounds (e.g., naphthalene, trichlorobenzene); pesticides; herbicides; PCBs; and metals.

Hydrogeology

Sauget Area 1 is located in the Mississippi River floodplain in an area referred to as the American Bottoms. The geology of the area is described as consisting of unconsolidated valley fill deposits (Cahokia Alluvium) overlying glacial outwash material (Henry Formation). In general, the permeability of the unconsolidated material increases with depth, with the outwash material being comprised of medium- to coarse-grained sand and gravel. The hydrogeologic conceptual model divides the unconsolidated water-bearing unit into three horizons: the shallow horizon (generally 15-30 ft deep), the middle horizon (generally 30-70 ft deep), and the deep horizon (generally 70-110 ft deep).

These unconsolidated deposits are underlain by limestone and dolomite bedrock.

3

Study Constituents

For this study, two classes of constituents were evaluated. The two constituent classes were selected based on prevalence and concentration in groundwater, and include:

- Volatile Organic Compounds (chlorinated and non-chlorinated), and
- Semi-Volatile Organic Compounds (chlorinated and non-chlorinated).

SOURCE MECHANISMS

Knowledge of which source mechanisms are active at a site is important for developing an accurate conceptual model of constituent fate and transport, and for developing appropriate remedial responses. Two source mechanisms that have the potential to be active at the Sauget site are leaching of unsaturated source materials and residual DNAPL dissolution (see Figure 1).
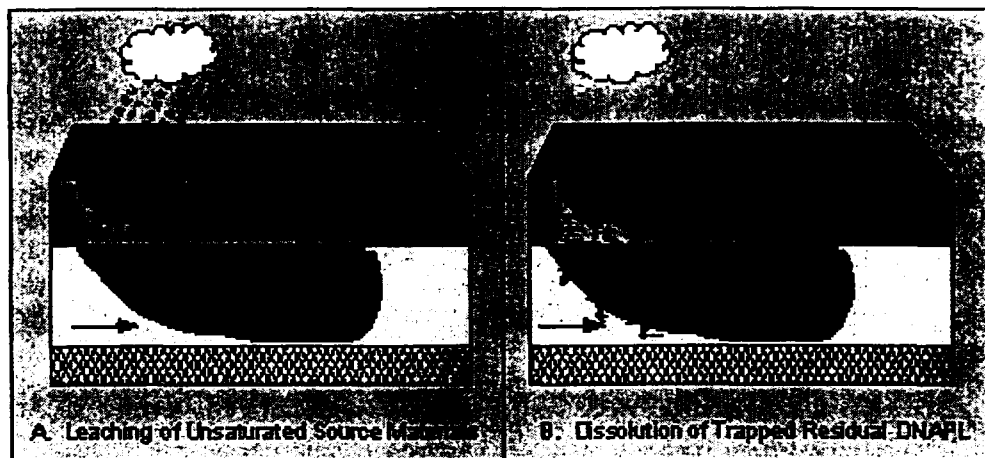

FIGURE 1. Two Potential Groundwater Source Mechanisms

Leaching of unsaturated source materials (see Panel A in Figure 1) results from infiltration of rainfall through near-surface source materials such as waste materials in the source areas and contaminated unsaturated soils. Residual DNAPL dissolution (see Panel B in Figure 1) occurs when soluble organic constituents dissolve from trapped residual DNAPL fingers and pools that entered the subsurface when the source area was active.

EVIDENCE OF SOURCE MECHANISMS

The available groundwater data were evaluated to help assess the likelihood that the two most likely source mechanisms are present at the site. The following six indicators were used:

General Indicators of Strong DNAPL Dissolution Processes:
- Indicator 1: Concentrations are generally increasing with depth.
- Indicator 2: Constituents are found deep in the water-bearing unit.
- Indicator 3: Concentrations are above 1% of the pure-phase solubility.
- Indicator 4: Results of EPA Quick Reference Fact Sheet "Estimating Potential for Occurrence of DNAPL at Superfund Sites," (Newell and Ross, 1992).

General Indicators of Strong Soil Leaching Processes:
- Indicator 5: Leachate concentrations (as indicated from TCLP tests of unsaturated waste materials) are greater than groundwater concentrations in the shallow horizon.
- Indicator 6: Concentrations in the shallowest horizon are greater than in deeper horizons.

To assess these indicators, groundwater constituent data were compiled (see Tables 1-2). Data from the groundwater transect (well AA-I-S1 for Site I) were used to evaluate constituent concentrations in the shallow horizon (< 30 ft deep) vs. middle horizon (30-70 ft deep) vs. deep horizon (70-110 ft deep) (see Table 1). Note that only the transect monitoring well closest to the source area was evaluated.

RESULTS

Indicator 1: An evaluation of groundwater data for Site I shows that the sum of *maximum* detectable VOCs + SVOCs in groundwater concentrations from the deep horizon is 47.5 mg/L, compared to only 22.1 mg/L in the shallow horizon (see Table 1). This trend is also seen in the majority of the individual VOC and SVOC constituents. For example, the maximum chlorobenzene concentration increases from 8.7 mg/L in the shallow horizon, to 20 mg/L in the middle horizon, and to 34 mg/L in the deep horizon. Of the five constituents with maximum concentrations greater than 1 mg/L, three (chlorobenzene, 1,2,4-trichlorobenzene, and 1,4-dichlorobenzene) have their maximum concentrations in the middle or deep horizon. The other two, cis/trans 1,2-dichloroethene and 4-chloroaniline, have the maximum concentration in the shallow horizon.

Indicator 2: Site constituents are found throughout the entire depth of the unconsolidated unit, from the water table surface to locations over 100 ft deep.

5

<u>Indicator 3:</u> Three site constituents (chlorobenzene, 1,4 dichlorobenzene, and fluoranthene) are found in concentrations that exceed 1% of each respective pure-phase solubility (see Table 1).

<u>Indicator 4:</u> Based on site historical data and observed groundwater concentrations, the EPA Fact Sheet "Estimating Potential for Occurrence of DNAPL at Superfund Sites," shows a "**High-Moderate**" Potential for DNAPL at Site I.

<u>Indicator 5:</u> Of the six constituents where a comparison could be made, five had higher concentrations in the groundwater than in the leachate from waste materials, suggesting that leaching was not responsible for the highest groundwater concentrations at Site I (see Table 2).

<u>Indicator 6:</u> As described above, only two of the five constituents with concentrations greater than 1 mg/L (cis/trans 1,2-dichloroethene and 4-chloroaniline) have their maximum concentrations in the shallow horizon.

KEY POINT: SITE I SOURCE MECHANISMS

DNAPL dissolution is a major source mechanism at Site I based on an analysis of the evaluated indicators. Dissolved constituent concentrations increase with depth, site constituents extend from the water table to the bottom of the water-bearing interval, and three constituents are found at concentrations that suggest the possible presence of non-mobile residual DNAPL.

Some leaching of unsaturated waste/soil materials may also be occurring, as some constituents such as 4-chloroaniline did not show increasing concentrations with depth. Overall, however, DNAPL dissolution appears to be the dominant source mechanism at Site I.

POTENTIAL FOR SOURCE REMEDIATION

Conceptual Model of Source

The following discussion summarizes our conceptual model of the DNAPL source located in the saturated zone beneath Site I:

- DNAPL is present as "fingers" and "pools" in the saturated zone extending from approximately 15 to 110 ft below the surface (see Figure 2 for a conceptual figure).

  Supporting Information: "Once penetration of the capillary fringe occurs, downward movement will continue until all the CHC (chlorinated hydrocarbon) solvent is present as suspended fingers (ganglia) in the porous media and/or as pools of CHC perched on low-permeability zones. Once a pool starts to form on top of a low-permeability layer somewhere above the bottom of the aquifer, a continued supply of CHC will cause (1) enlargement of the pool, (2) penetration of the layer, and/or (3) spawning of new downward-moving fingers at the perimeter of the layer." Johnson and Pankow (1992)
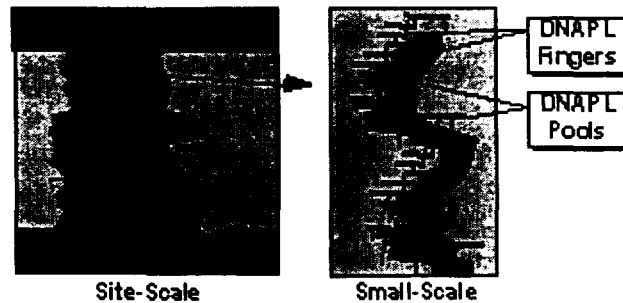
6

FIGURE 2.   Conceptual Model of DNAPL Source Zone

- Small horizontal pools of DNAPL are present throughout the entire vertical
  extent of the saturated zone, and not just at the bottom of the unit.

  Supporting Information: "In granular aquifers, small horizontal zones of residual or free-phase DNAPL need not be caused by particularly low permeability zones such as silt or clay. A minor contrast in grain size distribution and hence permeability, as from a coarse sand layer to a fine sand, causes variation in DNAPL entry pressure. A DNAPL will accumulate on the finer-grained layer while spreading laterally until it reaches the edge of the layer, or until the height of the free-product accumulation on the layer exceeds the entry pressure for the layer." Pankow and Cherry (1996)

- Much or most of the DNAPL mass is present in the trapped residual state that
  cannot be recovered by pumping.

  Supporting Information: "Note that after the continuous NAPL body has been converted to a residual form, the individual NAPL blobs are held very tightly in the porous media by capillary forces. Wilson and Conrad (1984) evaluated the force required to mobilize and completely sweep away residual blobs in porous media in terms of the hydraulic gradient a pumping system would have to generate to either 1) begin blob mobilization, or 2) mobilize all blobs in a porous medium. This relationship, presented as a graph of hydraulic conductivity vs. required hydraulic gradient, indicates that mobilization of NAPL blobs by pumping will occur only in very coarse porous media with a very high hydraulic gradient. The rest of the blobs will stay trapped in the porous media, serving as a long-term source of dissolved contaminants." (Wiedemeier et al., 1999)

  (Note: For the unconsolidated alluvial fill deposits at this site, Wilson and Conrad's analysis indicates that a gradient of 0.5 ft/ft would be required to begin to mobilize NAPL blobs. This is 500 times the current hydraulic gradient, and impossible to effect over the entire source area without extensive pumping and re-injection).

- It is extremely unlikely that any DNAPL that may be present at the site is still
  mobile or will become mobile under current conditions.

  Supporting Information: "Once the release of DNAPL into the subsurface ceases, subsurface movement of DNAPL also ceases soon thereafter, perhaps within weeks or months at

solvent sites. The resulting immobile DNAPL then exists in the DNAPL source zone as "residual" non-aqueous liquid and also possibly as "free-product" accumulations ponded on lower permeability layers within aquifers, or on the tops of aquitards. The free-product DNAPL will not become mobile again unless a release of more DNAPL causes further accumulation in the same zones, or unless there are changes in pressure in the surrounding water phase due to groundwater pumping or injection." Pankow and Cherry (1996)

- The presence of pools that can be pumped is relatively rare at DNAPL sites, and if such pools are found and pumped, only a small fraction of the total DNAPL in place is removed.

  Supporting Information: "In field investigations of sites where extensive solvent contamination exists, pools of free-product solvent are only rarely found, even when their existence is not in doubt." "It is the author's experience that chlorinated solvents with their high densities form thick pools only rarely." Pankow and Cherry (1996)

  "Therefore, in a practical sense, NAPL removal translates to recovery of a small percentage of NAPL at a site (i.e., whatever continuous NAPL can be collected)." Wiedemeier et al., (1999)

- The presence of DNAPL pools and fingers will only occupy a small fraction of the available pore space in the source zone.

  Supporting Information: "However, heterogeneity has a marked influence on the direction of DNAPL migration. A random distribution of permeability and displacement pressure will result in a highly erratic pattern of DNAPL flow..." "The remarkable sensitivity of DNAPL penetration to the capillary-hydraulic properties can be expected to result in highly complex, seemingly chaotic saturation distributions in the subsurface." "Even in the idealized case of a perfectly homogeneous medium, DNAPL can be expected to penetrate in the form of narrow, elongated distributions in which the mean saturation of DNAPL is small." Pankow and Cherry (1996)

- The source will persist for a long time.

  Supporting Information: "These calculations suggest that zones of residual DNAPL and especially pool DNAPL can persist in the subsurface and contribute to groundwater contamination for decades to centuries." "For most chlorinated solvents, the rate of dissolution of pools will be sufficiently slow that the DNAPL source zones will cause significant contamination of the groundwater for centuries or more." Pankow and Cherry (1996)

- Pumping can increase the rate that mass is removed from the source, but the removal efficiency will be much less than the removal efficiency for natural attenuation.

  Supporting Information: "However, the increase in mass removal (by pumping) will not be in proportion to the increase in the groundwater pumping rate because of limitations on the DNAPL dissolution kinetics, and because of further dilution with clean water from outside the source zone." Pankow and Cherry (1996)

KEY POINT: CONCEPTUAL MODEL FOR SOURCE

Most of the Site I DNAPL in the unconsolidated valley fill deposits is present as thin vertical fingers and small horizontal pools throughout the entire vertical extent of the water-bearing unit. Only a small fraction of the total DNAPL mass can ever be removed by pumping free-phase pools, if they are found. Under current conditions, the rest of the DNAPL is immobile, and will serve as a long-term continuing source of constituents to groundwater.

ESTIMATED NATURAL DISSOLUTION RATE

Natural Groundwater Flushing Rate

Separate hydraulic conductivity and hydraulic gradient data were developed for the shallow, middle, and deep horizons of the unconsolidated deposits.

The hydraulic conductivity estimates developed for the model were based on: 1) literature reports, and 2) preliminary analysis of RI/FS slug test data. The literature reference (Ritchey and Schicht, 1982) reported that the hydraulic conductivity for the unconsolidated material used for water supply in the American Bottoms area ranged from 5×10^{-2} to 1.4×10^{-1} cm/sec.

The analysis of RI/FS slug test data from Site I wells showed the following hydraulic conductivities:

Horizon	Site I (well ST-I-S) (cm/sec)
Shallow	4.5×10^{-3}
Middle	5.1×10^{-2}
Deep	1.3×10^{-1}

Using the data from the literature report, slug test results, and calibration work, the following hydraulic conductivities were used in the model:

Shallow Horizon:	1×10^{-2} cm/sec
Middle Horizon:	1×10^{-1} cm/sec
Deep Horizon:	1×10^{-1} cm/sec

Using RI/FS potentiometric surface maps provided by Roux Associates, Inc., the following hydraulic gradients were used in the model:

Shallow Horizon:	0.001 ft/ft
Middle Horizon:	0.001 ft/ft
Deep Horizon:	0.001 ft/ft

These values yield the following representative values for groundwater Darcy velocity at the site:

Shallow Horizon:	10.4 ft/yr
Middle Horizon:	104 ft/yr
Deep Horizon:	104 ft/yr

As shown by the data, the shallow horizon of the unconsolidated deposits is less permeable, and has a much lower groundwater velocity than the more coarse-grained middle and deep horizons.

The hydrogeologic conceptual model divides the unconsolidated water-bearing unit into three horizons: the shallow horizon (generally 15-30 ft deep), the middle horizon (generally 30-70 ft deep), and the deep horizon (generally 70-110 ft deep). Therefore the assumed saturated thicknesses for the shallow, middle, and deep units were: 15 ft, 40 ft, and 40 ft, respectively. When a 1400 ft wide source zone is assumed (the width of Site I perpendicular to groundwater flow), a naturally-occurring groundwater flushing rate of 168 gpm is obtained (3.1 gpm for the shallow unit, 82.5 gpm for the middle unit, and 82.5 gpm for the deep unit).

Natural Mass Removal Rate

The average total VOC + SVOC concentrations from the transect well closest to Site I (well AA-I-S1) are 13.3 mg/L, 21.9, mg/L, and 19.9 mg/L for the shallow, middle, and deep horizons, respectively. For this planning-level calculation, it was assumed that these concentrations extended throughout the entire width of the Site I source zone, a potential overestimation (however, if all other source removal calculations use the same assumptions, the relative results will be accurate). Therefore, the mass removal rate under natural conditions was estimated by multiplying average VOC + SVOC concentrations for each horizon by the flow for each horizon, and converting to a mass rate of kg/yr leaving the source zone (3.78 L/gal; 1440 min/day; 365 day/yr; 10^{-6} kg/mg). This calculation resulted in the following naturally-occurring mass removal rate totaling approximately 7000 kg/yr from all three horizons:

Shallow Horizon:	82 kg/yr
Middle Horizon:	3,613 kg/yr
Deep Horizon:	3,271 kg/yr
TOTAL:	6,966 kg/yr

KEY POINT: NATURAL MASS REMOVAL RATE

The natural mass removal rate from the Site I source zone is estimated to be 7000 kg/yr assuming uniform source concentrations throughout the source zone.

Assumed Flowrate From An Intensive Pump-and-Treat System

Three methods were evaluated to provide a planning-level estimate of the flowrate from an intensive pump-and-treat system at Site I (see Appendix A). First, an empirical well yield relationship (Driscoll, 1986) based on transmissivity, expected drawdown, and assumptions for other variables in the nonequilibrium (Jacob) equation was used. The second method was based on typical well yields from regional water supply wells as reported by Schicht (1965):

> "It is a general practice of industries and municipalities to place a well in operation and pump it at high rates, often about 1000 gpm."

The third method was based on evaluating specific capacity (well yield divided by drawdown) provided by Schicht (1965).

These calculation approaches suggest that an intensive pumping system for Site I could yield 1000–2500 gpm. For the purpose of this project, a value of 1500 gpm was used.

KEY POINT: GROUNDWATER FLOWRATE FROM INTENSIVE PUMPING

An intensive pump-and-treat system was assumed to have a yield of 1500 gpm.

EFFECT OF PUMPING GROUNDWATER

Because most of the DNAPL is trapped and cannot be removed by direct pumping, a groundwater pump-and-treat system will generally not remove DNAPL directly, but instead will slowly dissolve the DNAPL trapped in fingers and pools. While this dissolution process is relatively slow and inefficient, it will remove DNAPL mass.

Dissolution Kinetics for DNAPL Fingers and Pools

Several analyses have been performed to evaluate the effect of increased pumping rates on the DNAPL dissolution rate for both fingers and pools. In a key paper written by Hunt et al. in 1988, the authors developed relationships for the kinetics of dissolution in NAPL source zones. They evaluated laboratory studies and mass transfer approaches used in the chemical engineering literature, and derived dissolution expressions for residual NAPL ganglia (also called "fingers" or "blobs"). They concluded that:

"Ganglion lifetimes are weakly dependent on flow velocity such that to decrease the lifetime from 100 years to 10 years requires a three order of magnitude increase (x1000) in flow velocity."

In other words, increasing the groundwater pumping rate will increase the finger dissolution rate, but only slightly based on this relationship:

$$\frac{\text{mass transfer rate with pumping}}{\text{mass transfer rate without pumping}} = 10^{\frac{\log 10\left[\frac{Q_{pumping}}{Q_{natural}}\right]}{3}}$$

Using this NAPL dissolution relationships reported by Hunt et al. (1988), a 1500 gpm pumping system (a 8.9 times increase in the natural flow rate through the system) would result in a 8.9 fold *increase* in water flushed through the system, but a 4.3 fold *decrease* in effluent concentrations, resulting in a net increase in mass removed only by a factor of 2.1:

$$\frac{\text{mass transfer rate with pumping}}{\text{mass transfer rate without pumping}} = 10^{\frac{\log 10\left[\frac{1500 \text{ gpm}}{168 \text{ gpm}}\right]}{3}} = 2.1$$

The same type of concentration reduction is expected when higher groundwater flowrates are used to dissolve NAPL pools. Dissolution kinetic relationships developed by Johnson and Pankow (1992) indicate that the mass transfer rate (and pool lifetime) changes with the square root of groundwater velocity:

$$\text{Pool Dissolution Time (yrs)} = 2.43 \times 10^{-5} \, \rho \, C_{sat} \, [l_p^3/D_v \, v_d]^{0.5}$$

where:

ρ	=	DNAPL density (g/m^3)
C_{sat}	=	saturation concentration (g/m^3)
l_p	=	length of pool in direction of groundwater flow (m)
D_v	=	vertical dispersion coefficient (m^2/s)
v_d	=	Darcy velocity for groundwater (m/day)

Therefore, increasing the groundwater flowrate over a pool by a factor of 8.9 would result in an initial concentration *decrease* by a factor of 3.0 (approximately the square root of 8.9), and the overall *increase* in the mass removal rate by only a factor of 3.0.

Note that these theoretical expressions are supported by lab and field data (e.g., see Pankow and Cherry, 1996). Because source zones include a mixture of pools and fingers, it was assumed in this study that increasing the groundwater flowrate through the source zone by a factor of 8.9 (by pumping) would increase the mass transfer by a factor of 2.5 (the mid-point of finger value of 2.1 and pool values 3.0) when pumping was started. This is because groundwater concentrations decrease by a factor of 3.6 due to mass transfer effects. Note that after pumping is stopped, the concentrations would rebound and increase by a factor by the same amount (in the case of these calculations, by a factor of 3.6).

KEY POINT: EFFECT OF PUMPING GROUNDWATER ON CONCENTRATIONS

As shown by DNAPL dissolution expressions, the mass removal rate from a DNAPL source zone is only weakly dependent on the groundwater pumping rate. For example, if the flowrate though a DNAPL source zone is increased by a factor of 8.9 due to intensive pumping, the mass removal rate will only increase by a factor of 2.5 (a representative value for effects of pumping on DNAPL finger and DNAPL pool dissolution) because concentrations in the recovered groundwater would be reduced by a factor of 3.6 due to mass transfer effects.

Mass Removal Rate of Intensive Pump-and-Treat System

Under an intensive pumping scenario with an increase in natural flow (from 168 gpm to approximately 1500 gpm), the groundwater concentrations being removed from the source are expected to fall to between one-third to one-fifth of the observed concentrations under lower flow, natural conditions. Assuming a middle value of post-pumping concentrations that are 3.6 times smaller than the natural concentrations, the initial VOC + SVOC effluent concentrations from an intensive groundwater pump-and-treat system are estimated to be: 3.7 mg/L, 6.0 mg/L, and 5.5 mg/L for the shallow, middle, and deep units, respectively.

Therefore, under an intensive pump-and-treat scenario where 1500 gpm are being flushed through the Site I source zone (an 8.9-fold increase in the flushing rate), the initial mass removal rate is predicted to only increase by a factor of 2.5, from 7000 kg/yr to 17,500 kg/yr due to mass transfer effects related to DNAPL dissolution. Note that this is only the initial mass removal rate for the intensive pumping case, and that this concentration will drop slowly over time as mass is removed from the system.

KEY POINT: MASS REMOVAL RATE FROM INTENSIVE PUMPING

An intensive pump-and-treat system was estimated to have an initial mass removal rate of 17,500 kg/yr, accounting for both the increased flowrate through the system and decreased concentrations in groundwater.

Effect of Pumping on Source Lifetime

Estimating source longevity is a process involving considerable uncertainty, as the original mass in place, mass removal rate, and the change in the mass removal rate over time must all be known. While absolute estimates have a high level of uncertainty, the relative comparison of remediation alternatives can be made with more confidence. In the analysis below, the absolute values for source lifetime should be considered highly uncertain, while the relative comparisons should be considered more accurate.

Estimated Source Mass

A range of estimates of source mass were developed, assuming that the entire saturated zone below Site I is affected by DNAPL. Then the calculated mass removal rates for natural attenuation and an intensive pump-and-treat system were used to estimate source longevity.

Source mass is a function of source volume, the porosity, the residual saturation of DNAPL in the source zone, and the fraction of source volume containing DNAPL. At Site I, the estimated source volume is 1400 ft by 95 ft by 500 ft, or 66,500,000 ft³. Residual saturation (the fraction of open pore space occupied by DNAPL) values are typically assumed to be between 0.01 and 0.15 (see Pankow and Cherry, 1996), and a value of 0.05 was used for this analysis. A porosity of 0.35 was considered representative of the unconsolidated alluvial deposits at the site. Finally, it was assumed that 1% of the aquifer volume contains residual DNAPL.

Based on these assumptions, a planning-level estimate for the volume of DNAPL under Site I was estimated to be 87,000 gallons. Assuming an average density of 1.25 (based on an average of the density of chlorobenzene and 1,4-dichlorobenzene, two of the most commonly-found site constituents), the estimated mass of DNAPL is approximately 410,000 kg. Note that the actual mass may be more or less, but for the purpose of performing relative calculations of source longevity this value appeared to provide reasonable results.

KEY POINT: SITE I SOURCE MASS ESTIMATE

A planning-level source mass estimate of 410,000 kg of VOCs+SVOCs was estimated for the DNAPL source zone below Site I. There is considerable uncertainty in this estimate, with the actual mass potentially being higher or lower than 410,000 kg.

Source Decay Model

A simple source model, originally developed as part of the BIOSCREEN model (Newell et. al. 1996, EPA/600/R-96/087) and now being included as part of the BIOCHLOR model (Aziz et al., 2000, EPA/600/R-00/008) was used to estimate the lifetime of the groundwater source at Site I under different remediation options.

In this simple box model, the source zone is considered to be located in a box containing some mass of dissolvable contaminants. The rate at which contaminants leave the box is estimated from the rate at which flowing groundwater removes contaminants from the box. The time required to achieve a cleanup standard can then be estimated by comparing the mass of contaminants in the box vs. the time required to remove contaminants from the

box. To more closely match real-site conditions, the source concentration is assumed to decay over time, in proportion to the remaining source mass (Wiedemeier et al., 1999). With this assumption, the source concentration over time can be described using:

$$C_t = C_{so} \exp^{(-k_s t)}$$

where:

C_t	=	Source concentration at time t (mg/L)
C_{so}	=	Observed source concentration at t = 0 (mg/L)
t	=	Time (years)
k_s	=	Source decay coefficient (1/year)

(Note that this decay coefficient **is not** related in any way to first-order decay coefficients reported in the literature for natural attenuation, as the literature values typically represent decay half-lives from 0.1 to 10 years and represent biodegradation of dissolved contaminants in the plume *once they have left the source*. The source decay coefficient values represent how quickly a source zone is being depleted, and will usually have much longer half-lives, typically tens or hundreds of years.)

The source decay coefficient, representing how quickly the source is being depleted, can be derived using estimates of the source mass and rate that contaminants leave the source (Newell et al., 1996):

$$k_s = \frac{Q \cdot C_{so}}{M_o}$$

where:

Q	=	Groundwater flowrate through source zone (L/year)
C_{so}	=	Observed source concentration at time = 0 (mg/L)(or kg/L)
M_0	=	Dissolvable mass in source at time = 0 (mg)(or kg)

This model assumes that the only mass leaving the source zone is dissolved in the water flowing through the source zone. Note that Q and C_{so} are related; the thickness of the source zone should be matched with an appropriate average concentration for that entire depth horizon.

With a first-order source decay term, the source concentration at any time can be derived, providing the time required to reach any concentration:

$$t = -\frac{1}{k_s} \ln\left(\frac{C_t}{C_{so}}\right)$$

where:

t = Time required to reach concentration C_t (years)

Five Source Lifetime Cases

For this analysis, five different cases were evaluated using the source lifetime described above:

Case 1: Natural attenuation only (initial removal rate of 7000 kg/yr)

Case 2: 1 year of intensive pump-and-treat (initial removal rate of 17,500 kg/yr), followed by natural attenuation

Case 3: 5 years of intensive pump-and-treat (initial removal rate of 17,500 kg/yr), followed by natural attenuation

Case 4: 10 years of intensive pump-and-treat (initial removal rate of 17,500 kg/yr), followed by natural attenuation

Case 5: 30 years of intensive pump-and-treat (initial removal rate of 17,500 kg/yr), followed by natural attenuation

With this approach (see Appendix B), the following times to cleanup were estimated:

		Estimated Time to Cleanup (years)	% Reduction from Natural Attenuation Only
Case 1	Natural Attenuation Only	488	-
Case 2	1 Yr of Intensive Pump-and-Treat + Natural Attenuation	486	0.4% reduction
Case 3	5 Yrs of Intensive Pump-and-Treat + Natural Attenuation	480	2% reduction
Case 4	10 Yrs of Intensive Pump-and-Treat + Natural Attenuation	472	3% reduction
Case 5	30 Yrs of Intensive Pump-and-Treat + Natural Attenuation	441	10% reduction

Figure 3 shows a comparison of source concentrations vs. time for two of the six cases.

**Source Concentration vs. Time Analysis
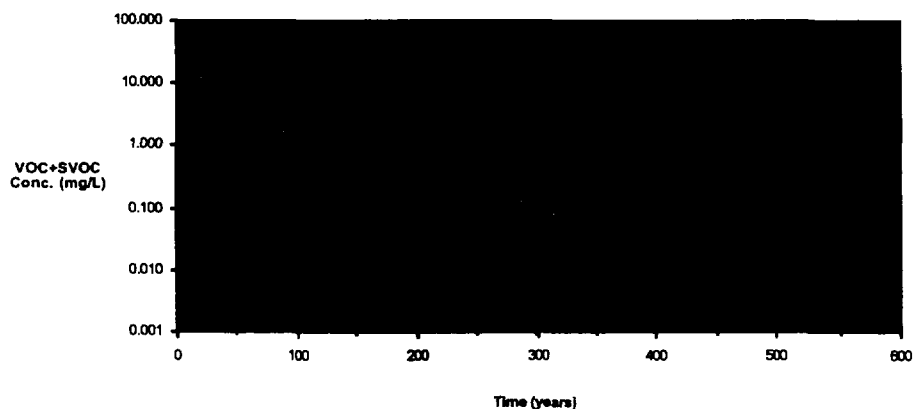Sauget Area 1, Site I**

FIGURE 3. Source concentration vs. time graphs for Case 1 (Natural Attenuation Only) and Case 5 (30 Years of Intensive Pump-and-Treat + Natural Attenuation). For Case 1, concentrations start at 20 mg/L and decline as a first order decay relationship over time. For Case 5, the source concentration starts at 20 mg/L, but concentrations are reduced by a factor of 3.6 due to mass transfer effects caused by the almost 9 times increase in groundwater flow through the source zone. After 30 years, pumping is stopped, groundwater flow is restored to natural conditions, and mass transfer effects cause an increase in concentration by a factor of 3.6 (the "rebound" effect). Overall, the source modeling exercise shows that with the source assumptions described in the text, the time required to restore groundwater is reduced only slightly by 30 years of intensive pumping, from 488 years to 441 years (10% reduction).

Sensitivity Analysis

The source lifetime analysis has several areas of uncertainty, and should be used to evaluate relative differences between remediation alternatives rather than to provide an absolute source lifetime estimate. Significant sources of uncertainty include:

* *The assumption that concentrations observed in well AA-I-S1 extend throughout the entire 1400 ft source width of Site I.* If some sections of the 1400 ft source width of Site I are lower concentration, the following impact on the source lifetime is expected: 1) for the natural attenuation case, the overall source lifetime estimates will not change as both the removal rate and the mass in the source are functions of the source width; and 2) for the pumping case, some reduction in overall source lifetime is expected as source mass is dependent on source width but removal rate is not (it is dependent on pumping rate and expected concentrations).

17

- *The assumptions that the source is represented by a residual DNAPL saturation of 0.05 and that 1% of the source zone is impacted by DNAPL residual.* These assumptions have a great deal of uncertainty (the literature reports that residual saturations can be as high as 0.50), and were selected in part to yield source lifetimes in the range of several hundreds of years to match the source conceptual model discussed above. If the source is much smaller than the estimated 410,000 kg of VOCs+SVOCs, then the impact of a pumping system will be greater, and greater than a 1% to 10% reduction in source lifetime will be realized. If the source mass is only 41,000 kg (an unlikely event based on the persistence of the source to date), then an intensive pump-and-treat system is predicted to reduce the source lifetime by from 49 years (natural attenuation alone) to 22 years (intensive pumping). Conversely, if the mass is greater, a pump-and-treat system will have less of an effect.

Other, potentially less significant sources of uncertainty are:

- *The assumption that concentrations under a pumping scenario will be smaller than concentrations observed under natural flow conditions.* While there is uncertainty in the actual amount, it has been demonstrated in lab studies and the field that increasing the flowrate through a DNAPL source zone will result in lowered concentrations (for example, see Pankow and Cherry, 1996). Therefore we expect some concentration reduction with a pump-and-treat scenario.

- *The assumption that the flow throughout each interval is uniform and that the concentration in each interval can be calculated by averaging each sample point.* These assumptions were used in the mass removal calculation. While there may be some uncertainty in these assumptions, the large number of vertical samples reduces the potential error.

- *The assumption of a first-order decay relationship for the source dissolution rate.* This assumption is based on observations about source decay, and is now used in two EPA peer-reviewed models, BIOSCREEN and BIOCHLOR. While the exact source concentrations curve may not be exactly first order, it will almost certainly fit a first-order decay curve better than assuming constant source concentrations until the source is exhausted. (Note that the use of the first order decay model for the source does not mean that literature-based first-order decay constants for dissolved constituents were used. A source decay constant is based on removal rate and initial source mass, while a biodegradation rate is based on how fast concentrations decay after they leave the source. This study used a source decay approach, and did not use biodegradation rates to estimate source lifetime).

- *No availability effects related to desorption of constituents at low concentrations have been considered.* Slow desorption of non-available fraction of constituents sorbed to aquifer materials will likely reduce the efficiency of any flushing

18

technology. More pronounced effects may be observed for intensive pumping scenarios.

Additional Analysis

A similar analysis was performed for Sites G/H/L using the same calculation approach as was used for Site I (Appendix B). Two cases were performed, and show little impact from a five-year intensive pumping program:

		Estimated Time to Cleanup (years)	% Reduction from Natural Attenuation Only
Case 6	Natural Attenuation Only – Sites G/H/L	434	-
Case 7	5 Yrs of Intensive Pump-and-Treat + Natural Attenuation	427	2% reduction

An evaluation of other constituents present in Sites G/H/I/L groundwater, such as herbicides, pesticides, dioxins, and metals indicates that some constituents will like achieve cleanup goals faster than the VOCs + SVOCs analyzed for this source report, and others may take longer. Ratios of the maximum observed concentrations at Area 1 vs. the Illinois Class I standard for representative constituents provide a general indication of how quickly various constituents may achieve cleanup goals:

CONSTITUENT (Constituent Class)	MAXIMUM CONCENTRATION IN GROUNDWATER (ug/L)	ILLINOIS CLASS I STANDARD (ug/L)	RATIO OF MAX. CONC. / ILLINOIS CLASS I STD.
Chlorobenzene (VOC)	34,000	100	340
2,4-dichlorobenzene (SVOC)	14,000	75	187
Alpha-BHC (Herbicide)	72	0.03	2400
2,4-D (Pesticide)	190	70	2.7
Total PCBs (PCB)	12	0.5	24
Cu (Metal)	3000	650	4.6
Ni (Metal)	7800	100	78
Pb (Metal)	3600	7.5	480

Zn (Metal)	33,000	5000	6.6

On the basis of this general evaluation, alpha-BHC may take longer to achieve cleanup goals than the VOCs+SVOCs, while 2,4-D may take less time. Other factors, such as the mass of each constituent in the source zone and the constituent-specific fate and transport process will determine the ultimate time required to remediate the Area 1 source zones.

KEY POINT: ESTIMATED SOURCE LIFETIMES FOR SEVEN CASES

A planning level source lifetime calculation was done to estimate the relative performance of various remediation schemes. This analysis, while not providing high-confidence estimates of the absolute time to cleanup, does indicate that with an assumed mass of 410,000 kg of VOCs + SVOCs in the saturated zone below Site I, intensive pumping over a 1 to 30 year period does not appear to have an appreciable effect on overall source lifetime (i.e., $\leq 10\%$ reduction). Similar limitations are expected at Sites G/H/L as well.

CONCLUSIONS

Based on the overall groundwater source evaluation at Site I of Sauget Area 1, DNAPL dissolution appears to be the dominant source mechanism. Planning level source lifetime calculations indicate that intensive groundwater pumping will not have an appreciable effect on the overall source lifetime at Site I or at Site G/H/L.

REFERENCES

Aziz, C.E., C.J. Newell, J.R. Gonzales, P.E. Haas, T.P. Clement, and Y. Sun, 2000. BIOCHLOR Natural Attenuation Decision Support System, User's Manual Version 1.0, U.S. EPA, Office of Research and Development, www.gsi-net.com, EPA/600/R-00/008, Washington D.C., January, 2000.

Driscoll, F., 1986. Ground Water and Wells, 2nd Ed., Johnson Division, St. Paul, Minnesota.

Hunt, J.R., N. Sitar, and K.D. Udell, 1988. "Nonaqueous Phase Liquid Transport and Cleanup", Water Res. Research, Vol. 24, No. 8, 1988.

Johnson, R.L., and J.F. Pankow, 1992. "Dissolution of Dense Chlorinated Solvents in Groundwater, 2. Source Functions for Pools of Solvents", Environ. Science and Technology, v. 26, no. 5, p. 896-901.

Newell, C.J., J. Gonzales, and R. McLeod, 1996. BIOSCREEN Natural Attenuation Decision Support System, Version 1.3, U.S. Environmental Protection Agency, EPA/ 600/R-96/087, www.epa.gov/ada/kerrlab.html

Newell, C.J. and R. Ross, 1992. Estimating Potential for Occurrence of DNAPL at Superfund Sites, EPA Quick Reference Fact Sheet (EPA Publication 9355.4-07FS), January 1992.

Pankow, J. F. and J. A. Cherry, 1996. Dense Chlorinated Solvents and other DNAPLs in Groundwater, Waterloo Press, Waterloo, Ontario, 1996.

Ritchey, J. D., and R.J. Schicht, 1982. "Ground-Water Management in the American Bottoms, Illinois, State, County, Regional and Municipal Jurisdiction of Ground-Water Protection," Proceedings of the Sixth National Ground-Water Quality Symposium, Atlanta, Georgia, Sept. 22-24, EPA/National Water Well Association, Columbus, Ohio.

Schicht, R.J., 1965. Ground-Water Development in East St. Louis Area, Illinois, Report of Investigation 51, Illinois State Water Survey, Urbana, Illinois.

Wiedemeier, T.H., H.S. Rifai, C.J. Newell, and J.T. Wilson, 1999. Natural Attenuation of Fuel Hydrocarbons and Chlorinated Solvents, John Wiley and Sons, New York, New York.

Wilson, J.L. and S.H. Conrad, 1984. "Is Physical Displacement of Residual Hydrocarbons a Realistic Possibility In Aquifer Restoration?" National Water Well Association, Proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water Conference, Houston, Texas, November 1984.

GROUNDWATER SERVICES, INC.

TABLE 1
SUMMARY OF SITE I GROUNDWATER CONCENTRATIONS BY DEPTH AND COMPARISON TO CONSTITUENT SOLUBILITY
Sampling Period: November to December 1999

Solutia Inc.
Area 1, Sauget and Cahokia, Illinois

VOCs				
1,1-Dichloroethane	0.96	<0.5	<1.0	5,060
1,1-Dichloroethene	0.032 J	<0.5	<1.0	2,250
Benzene	**0.62**	0.19	0.14 J	1,750
Chlorobenzene	8.7	20.0	**34.0**	_472_
cis/trans-1,2-Dichloroethene	**1.2**	0.31	0.001 J	3,500 (7)
Ethylbenzene	**0.87**	0.27	0.074	169
Tetrachloroethene	<0.5	<0.5	0.001 J	200
Toluene	0.018 J	**0.086 J**	0.00089 J	526
Vinyl Chloride	**0.97**	0.32	0.0012 J	2,760
Xylenes, total	<0.5	0.023 J	0.014	186
SVOCs				
1,2,4-Trichlorobenzene	<0.01	<0.5	2.7	300
1,2-Dichlorobenzene	0.13	0.32 J	0.5	156
1,3-Dichlorobenzene	0.11	**0.29 J**	0.150 J	NA
1,4-Dichlorobenzene	4.4	10 D	9.7 D	_73.8_
2,4,5-Trichlorophenol	<0.01	<0.5	0.0018 J	1,200
2,4-Dichlorophenol	<0.01	0.042	0.047 J	4,500
2-Chlorophenol	0.0055 J	0.039	**0.052**	22,000
2-Methylnaphthalene	<0.01	<0.5	0.0013 J	NA
2-Methylphenol (o-cresol)	<0.01	0.003 J	<0.4	26,000
4-Chloroaniline	**4.1 D**	1.7 D	0.018	5,300
Acenaphthene	<0.01	<0.5	0.00033 J	4.24
Carbazole	0.0014 J	0.013	**0.013**	7.48
Di-n-butylphthalate	<0.01	0.00034 J	0.00051 J	11.2
Dibenzofuran	<0.01	0.019 J	<0.4	NA
Diethylphthalate	<0.01	0.0051 J	<0.4	1,080
Fluoranthene	<0.01	0.022 J	<0.4	_0.206_
Hexachlorobenzene	<0.01	<0.5	0.001 J	6.2
N-Nitrosodiphenylamine	0.0053	**0.028**	0.02	35.1
Naphthalene	0.0042 J	0.024	**0.066**	31
Phenanthrene	<0.01	**0.089 J**	0.0013 J	NA
Phenol	<0.01	0.0044 J	<0.4	82,800
bis(2-chloroethyl)ether	0.0011 J	<0.5	<0.4	17,200
bis(2-ethylhexyl)phthalate	0.00069 J	<0.09	<0.072	0.34
Total Detected Conc. (mg/L)	**22.1**	**33.8**	**47.5**	

Notes:
1) Table includes only those compounds detected in at least one groundwater sample for each constituent class. Comparison to solubility includes groundwater sampled at any depth in source area monitoring well.
2) Groundwater samples included are from nearest source area monitoring well only (i.e., AA-I-S1).
3) J = Estimated value. D = Diluted sample. NA = Not available.
4) Bold type denotes maximum groundwater concentration by depth.
5) Underlined bold italics type denotes maximum groundwater concentration exceeds 1% of constit. solubility.
6) Lowest solubility of cis/trans-1,2-Dichloroethene pair indicated.
7) Solubility data from Illinois Tiered Approach to Corrective Action Objectives (TACO).
8) For comparison purposes, non-detectable concentrations are taken as the detection limit shown.

GROUNDWATER SERVICES, INC.

TABLE 2
SUMMARY OF SITE I GROUNDWATER CONCENTRATIONS BY DEPTH VERSUS
TCLP WASTE DATA
Sampling Period: November to December 1999

Solutia Inc.
Area 1, Sauget and Cahokia, Illinois

VOCs					
1,1-Dichloroethane	0.96	<0.5	<1.0	NA	-
1,1-Dichloroethene	**0.032 J**	<0.5	<1.0	<0.02	GW
Benzene	**0.62**	0.19	0.14 J	0.14	GW
Chlorobenzene	8.7	20.0	**34.0**	8.9	GW
cis/trans-1,2-Dichloroethene	1.2	0.31	0.001 J	NA	-
Ethylbenzene	0.87	0.27	0.074	NA	-
Tetrachloroethene	<0.5	<0.5	0.001 J	0.29	-
Toluene	0.018 J	0.086 J	0.00089 J	NA	-
Vinyl Chloride	**0.97**	0.32	0.0012 J	<0.04	GW
Xylenes, total	<0.5	0.023 J	0.014	NA	-
SVOCs					
1,2,4-Trichlorobenzene	<0.01	<0.5	2.7	NA	-
1,2-Dichlorobenzene	0.13	0.32 J	0.5	NA	-
1,3-Dichlorobenzene	0.11	0.29 J	0.150 J	NA	-
1,4-Dichlorobenzene	4.4	**10 D**	9.7 D	1.3	GW
2,4,5-Trichlorophenol	<0.01	<0.5	0.0018 J	**1.4**	TCLP
2,4-Dichlorophenol	<0.01	0.042	0.047 J	NA	-
2-Chlorophenol	0.0055 J	0.039	0.052	NA	-
2-Methylnaphthalene	<0.01	<0.5	0.0013 J	NA	-
2-Methylphenol (o-cresol)	<0.01	0.003 J	<0.4	0.014 J	-
4-Chloroaniline	4.1 D	1.7 D	0.018	NA	-
Acenaphthene	<0.01	<0.5	0.00033 J	NA	-
Carbazole	0.0014 J	0.013	0.013	NA	-
Di-n-butylphthalate	<0.01	0.00034 J	0.00051 J	NA	-
Dibenzofuran	<0.01	0.019 J	<0.4	NA	-
Diethylphthalate	<0.01	0.0051 J	<0.4	NA	-
Fluoranthene	<0.01	0.022 J	<0.4	NA	-
Hexachlorobenzene	<0.01	<0.5	0.001 J	<0.05	-
N-Nitrosodiphenylamine	0.0053	0.028	0.02	NA	-
Naphthalene	0.0042 J	0.024	0.066	NA	-
Phenanthrene	<0.01	0.089 J	0.0013 J	NA	-
Phenol	<0.01	0.0044 J	<0.4	NA	-
bis(2-chloroethyl)ether	0.0011 J	<0.5	<0.4	NA	-
bis(2-ethylhexyl)phthalate	0.00069 J	<0.09	<0.072	NA	-

GW Conc. Greater	5
TCLP Conc. Greater	1

Notes:

1) Table includes only those compounds detected in at least one groundwater sample for each constituent class.
   Comparison to TCLP waste concentration includes groundwater sampled at any depth in source area monitoring well.
2) Groundwater samples included are collected from nearest source area monitoring well only (i.e., AA-I-S1).
3) J = Estimated value. D = Diluted sample.
4) **Underlined bold type** denotes maximum groundwater concentration or TCLP concentration.
5) TCLP waste data from unsaturated waste samples.
6) NA = Not analyzed.
7) For comparison purposes, non-detectable concentrations are taken as the detection limit shown.

APPENDIX A
DESIGN PUMPING RATE OF HYDRAULIC CONTAINMENT WELLS
Groundwater Alternative D, Intensive Pumping, Sites G, H, I, and L
Sauget Area 1, Sauget and Cahokia, Illinois

PROBLEM: What is estimated pumping rate and number of wells for intensive pumping system for Site I + Sites G/H/L plume?

ASSUMPTIONS:

K = 0.1 cm/sec for middle, deep horizon

b = 80 ft (40 ft middle horizon, 40 ft deep horizon)

i = 0.001 ft/ft

Available drawdown (s) = 15 ft (thickness of shallow unit) (this equals thickness of shallow saturated horizon)

METHOD: Use three different methods to develop a basis for flowrates for an intensive pumping system for the combined Site I + Site G/H/L plume areas.

Method 1. First, an empirical well pumping rate relationship (Driscoll, 1986) based on transmissivity, expected drawdown, and assumptions for other variables in the nonequilibrium (Jacob) equation was used. For this site, a transmissivity of 170,000 gpd/ft was calculated (based on an assumed hydraulic conductivity of 0.1 cm/sec and a saturated thickness of 80 ft for the combined middle and deep horizons).

For unconfined units:

$$\frac{Q}{s} = \frac{T}{1500} \qquad \text{(Eqn. 3, Q in gpm, s in ft, T in gpd/ft)}$$

$$Q(gpm) = \frac{\left(T\,\frac{gpd}{ft}\right)(s\ ft)}{1500}$$

$$T = (K)(b_T)$$

$$T = \left(0.1\frac{cm}{sec}\right)\left(\frac{86400\,sec}{day}\right)\left(\frac{in}{2.54\,cm}\right)\left(\frac{ft}{12\,in}\right)(80ft)\left(\frac{7.48\,gal}{ft^3}\right)$$

$$T = 170,000\,gpd/ft$$

$$Q(gpm) = \frac{\left(170,000\,\frac{gpd}{ft}\right)(15ft)}{1500}$$

$$Q = 1700\,gpm$$

so that:

Q = 1700 gpm for pumping from a regional pumping well

<u>Method 2.</u>   Schicht (1965) reports that "It is a general practice of industries and municipalities to place a well in operation and pump it at high rates, often about 1000 gpm." Therefore based on this method:

Q = 1000 gpm for pumping from a regional pumping well

<u>Method 3.</u>   Schicht also reports the specific capacity from three wells in T2N, R10W (where Area 1 is located) as being 152.5, 188, and 158 gpm/ft, respectively. By averaging these specific capacities (166 gpm/ft), and multiplying by an assumed drawdown of 15 ft, a pumping rate of **2490 gpm** is obtained. As would be expected, use of specific capacities results in a wide range of predicted well pumping rates due to the effects of well construction, well condition, and local hydrogeologic conditions.

Q = 2500 gpm for pumping from a regional pumping well

RESULT: These calculation approaches suggest that a regional pumping well could yield from 1000 to 2500 gpm in the Area 1 location.

Therefore, it was assumed that the total pumping rate of any intensive pumping system would also be in this range, although the flow would be distributed among several wells. Therefore the following conceptual design was developed:

Qtotal   =   **1500 gpm total flowrate** (based on lower-middle range of flowrate estimates to be conservative)

APPENDIX B
RELATIVE SOURCE LIFETIME OF AREA I UNDER NATURAL ATTENUATION VS. INTENSIVE PUMP AND TREAT
Groundwater Alternative D, Intensive Pumping, Sites G, H, I, and L
Sauget Area 1, Sauget and Cahokia, Illinois

I. SOURCE LIFETIME CALCULATION: SITE I

PROBLEM: What is relative source lifetime of Site I under natural attenuation vs. intensive pump and treat conditions?

ASSUMPTIONS:

1. $\text{Source Volume} = (1400ft)(500ft)(95ft)\left(7.48\frac{gal}{ft^3}\right)(0.35)(0.05)(0.01) = 87,000\,gals$

   $\text{Source Mass} = (87,000\,gal)\left(\frac{3.78L}{gal}\right)\left(\frac{1.25kg}{L}\right) = 410,000\,kg$

   Where: width = 1400 ft; length = 500 ft; sat. thickness = 95 ft; porosity = 0.35; assumed residual saturation = 0.05; fraction of source containing residual saturation = 0.01. (see text)

2. Current Mass Removal Rate: 7000 kg/yr (Natural Attenuation) (see text)
   Initial Intensive Pumping Removal Rate: 17,500 kg/yr (Intensive Pump-and-Treat) (see text).

3. Case 1   Natural Attenuation Only – Site I
   Case 2   1 Yr of Intensive Pump-and-Treat + Natural Attenuation – Site I
   Case 3   5 Yrs of Intensive Pump-and-Treat + Natural Attenuation – Site I
   Case 4   10 Yrs of Intensive Pump-and-Treat + Natural Attenuation – Site I
   Case 5   30 Yrs of Intensive Pump-and-Treat + Natural Attenuation – Site I

4. Starting concentration under natural conditions: 20 mg/L (representative of middle and deep units in 1999). Starting concentration under pumping conditions: 5.5 mg/L (due to mass-transfer effects for deep and middle units; factor of 3.6 reduction).

5. Assumed ending concentration: 0.005 mg/L (MCL for several constituents).

MODEL:

$\dfrac{C_{(t)}}{C_{(now)}} = e^{-k_s t}$ (from BIOSCREEN and BIOCHLOR models; see text)

$$k_s = \frac{\text{Mass Removal Rate}(kg/yr)}{\text{Mass}(kg)} \qquad (k_s = \text{source decay constant})$$

$$t(yr) = \frac{-\ln\left(\dfrac{C_t}{C_{now}}\right)}{k_s}$$

Model Applied to Case 1: Natural Attenuation Only

$$t(yr) = \frac{-\ln\left(\dfrac{0.005}{20}\right)}{0.017}$$

RESULT (Case 1): $t = 488\ years$

Model Applied to Case 2: Intensive Pump and Treat With 1 Year of Pumping

$$k_s = \frac{17,500\dfrac{kg}{yr}}{410,000\,kg} = 0.043\,yr^{-1}$$

$$\frac{C_{1yr}}{C_{now}} = e^{-k_s\,t}$$

$$\frac{C_{1yr}}{5.5\,mg/L} = e^{-(0.043\,yr^{-1})(1yr)}$$

$$C_{1\,yr} = 5.27\ mg/L$$

Time to cleanup after 1 yr of pumping is finished, with 3.6-times increase in concentration due to rebound (5.27 mg/L * 3.6 = 19.0 mg/L).

$$\frac{0.005\,mg/L}{19.0\,mg/L} = e^{-(0.017\,yr^{-1})(t\,yrs)}$$

$$t = \frac{-\ln\left(\dfrac{0.005}{19.0}\right)}{0.017}$$

$$t = 485\,years$$

RESULT (Case 2): Total time to cleanup (Intensive Pump-and-Treat for 1 yr) = 1 + 485 = **486 years**

Model Applied to Case 3: Intensive Pump and Treat With 5 Years of Pumping

$$k_S = \frac{17,500\frac{kg}{yr}}{410,000\,kg} = 0.043\,yr^{-1}$$

$$\frac{C_{5yrs}}{C_{now}} = e^{-k_S t}$$

$$\frac{C_{5\ yrs}}{5.5\ mg/L} = e^{-(0.043\ yr^{-1})(5\ yrs)}$$

$$C_{5\,yrs} = 4.44\,mg/L$$

Time to cleanup after 5 yrs of pumping is finished, with 3.6-times increase in concentration due to rebound (4.44 mg/L * 3.6 = 16.0 mg/L).

$$\frac{0.005\,mg/L}{16.0\,mg/L} = e^{-(0.017yr^{-1})(t\,yrs)}$$

$$t = \frac{-\ln\left(\frac{0.005}{16.0}\right)}{0.017}$$

$$t = 475\,years$$

RESULT (Case 3): Total time to cleanup (Intensive Pump-and-Treat for 5 yrs) = 5 + 475 = **480 years**

Model Applied to Case 4: Intensive Pump and Treat With 10 Years of Pumping

$$k_s = \frac{17,500\frac{kg}{yr}}{410000\,kg} = 0.043 yr^{-1}$$

$$\frac{C_{10yrs}}{C_{now}} = e^{-k_s t}$$

$$\frac{C_{10yrs}}{5.5\,mg/L} = e^{-(0.043 yr^{-1})(10yrs)}$$

$$C_{10\,yrs} = 3.58\,mg/L$$

Time to cleanup after 10 yrs of pumping is finished, with 3.6-times increase in concentration due to rebound (3.58 mg/L * 3.6 = 12.9 mg/L).

$$\frac{0.005\,mg/L}{12.9\,mg/L} = e^{-(0.017 yr^{-1})(t\,yrs)}$$

$$t = \frac{-\ln\left(\frac{0.005}{12.9}\right)}{0.017}$$

$$t = 462\,years$$

RESULT (Case 4): Total time to cleanup (Intensive Pump-and-Treat for 10 yrs) = 10 + 462 = **472 years**

Model Applied to Case 5: Intensive Pump and Treat With 30 Years of Pumping

$$k_s = \frac{17,500\frac{kg}{yr}}{410000\,kg} = 0.043 yr^{-1}$$

$$\frac{C_{30yrs}}{C_{now}} = e^{-k_s t}$$

$$\frac{C_{30yrs}}{5.5\,mg/L} = e^{-(0.043 yr^{-1})(30yrs)}$$

$$C_{30yrs} = 1.51\,mg/L$$

Time to cleanup after 30 yrs of pumping is finished, with 3.6-times increase in concentration due to rebound (1.51 mg/L * 3.6 = 5.4 mg/L).

$$\frac{0.005\,mg/L}{5.4\,mg/L} = e^{-\left(0.017yr^{-1}\right)\left(t\,yrs\right)}$$

$$t = \frac{-\ln\left(\frac{0.005}{5.4}\right)}{0.017}$$

$$t = 411\,years$$

RESULT (Case 5): Total time to cleanup (Intensive Pump-and-Treat for 30 yrs) = 30 + 411 = **441 years**

CONCLUSION: Comparison of Cleanup Times – Site I

Case 1	Natural Attenuation Only	488 years
Case 2	1 Yr of Intensive Pump-and-Treat + Natural Attenuation	486 years
Case 3	5 Yrs of Intensive Pump-and-Treat + Natural Attenuation	480 years
Case 4	10 Yrs of Intensive Pump-and-Treat + Natural Attenuation	472 years
Case 5	30 Yrs of Intensive Pump-and-Treat + Natural Attenuation	441 years

II. SOURCE LIFETIME CALCULATION: SITES G/H/L

PROBLEM: What is relative source lifetime of Sites G/H/L under natural attenuation vs. intensive pump and trea conditions?

ASSUMPTIONS:

1. Assume Sites G/H/L together have approximately same dimensions as Site I, with 1% of the starting mass as Site I, because VOC+SVOC concentrations are much lower leaving Sites G/H/L (~ 0.20 mg/L) than Site I (~ 20 mg/L).

2. Assume ratio of source mass at Sites G/H/L and Site I are proportional to ratio of representative concentrations and width parallel to groundwater flow leaving Sites G/H/L and Site I.

$$\text{Source Mass} = \left(\frac{\text{representative conc. Sites G/H/L mg/L}}{\text{representative conc. Site I mg/L}}\right)(\text{Est. Mass Site I kg})$$

$$= \left(\frac{0.20 \text{ mg/L}}{20 \text{ mg/L}}\right)(410{,}000 \text{ kg})$$

$$= 4100 \text{ kgs}$$

3. **Current Mass Removal Rate:** Assume 1% of Site I mass removal rate based on ratio of representative concentration at Site I (20 mg/L VOC+SVOC) to representative concentration at Sites G/H/L (0.20 mg/L VOC+SVOC).

Natural Source Removal Rate =

$$\left(\frac{\text{representative conc. Sites G/H/L mg/L}}{\text{representative conc. Site I mg/L}}\right)\left(\frac{\text{Width Sites G/H/L}}{\text{Width Site I}}\right)(\text{Est. Mass Removal Rate Site I kg/y})$$

$$= \left(\frac{0.20 \text{ mg/L}}{20 \text{ mg/L}}\right)\left(\frac{750 \text{ ft}}{1400 \text{ ft}}\right)(7000 \text{ kg/y})$$

$$= 35 \text{ kg/yr}$$

Use Initial Intensive Pumping Removal Rate of 2.5 times 34 kg/yr (Intensive Pump-and-Treat= 87.5 kg/yr

4. Run analysis for two cases:

    Case 6   Natural Attenuation Only – Site G/H/L

    Case 7   5 Yrs of Intensive Pump-and-Treat + Natural Attenuation – Site G/H/L

5. Starting concentration under natural conditions: 0.20 mg/L (representative of middle and deep units in 1999). Starting concentration under pumping conditions: 0.056 mg/L (due to mass-transfer effects for middle and deep units; factor of 3.6 reduction).

6. Assumed ending concentration: 0.005 mg/L (MCL for several constituents).

MODEL:

$$\frac{C_{(t)}}{C_{(now)}} = e^{-k_s t} \quad \text{(from BIOSCREEN and BIOCHLOR models; see text)}$$

$$k_s = \frac{Mass\ Removal\ Rate(kg/yr)}{Mass\ (kg)} \quad (k_s = \text{source decay constant})$$

$$t(yr) = \frac{-\ln\left(\frac{C_t}{C_{now}}\right)}{k_s}$$

Model Applied to Case 6: Natural Attenuation Only

$$k_s = \frac{35\frac{kg}{yr}}{4100kg} = 0.0085\ yr^{-1}$$

$$t(yr) = \frac{-\ln\left(\frac{0.005}{0.2}\right)}{0.0085}$$

RESULT (Case 6):   *t = 434 years*

Model Applied to Case 7: Intensive Pump and Treat With 5 Years of Pumping

$$k_s = \frac{87.5\frac{kg}{yr}}{4100kg} = 0.02\ 1yr^{-1}$$

$$\frac{C_{1yr}}{C_{now}} = e^{-k_s t}$$

Starting concentration under pumping conditions: 0.056 mg/L (due to mass-transfer effects for deep and middle units; factor of 3.6 reduction).

$$\frac{C_{5yr}}{0.056\ mg/L} = e^{-(0.02\ 1yr^{-1})(5yrs)}$$

$$C_{5\ yr} = 0.050\ mg/L$$

Time to cleanup after 5 yrs of pumping is finished, with 3.6-times increase in concentration due to rebound (0.050 mg/L * 3.6 = 0.18 mg/L).

**GROUNDWATER
SERVICES, INC.**

$$\frac{0.005\,mg/L}{0.18\,mg/L} = e^{-\left(0.00085\,yr^{-1}\right)\left(t\,yrs\right)}$$

$$t = \frac{-\ln\left(\frac{0.005}{0.18}\right)}{0.0085}$$

$$t = 422\,years$$

RESULT (Case 7): Total time to cleanup (Intensive Pump-and-Treat for 5 yrs) = 5 + 422 = **427 years**

CONCLUSION: Comparison of Cleanup Times – Sites G/H/L

Case 6   Natural Attenuation Only – Sites G/H/L...434 years

Case 7   30 Yrs of Intensive Pump-and-Treat + Natural Attenuation –

              Sites G/H/L ....427 years